

PCT/EP 98/03583
09/445844

REC'D 12 AUG 1998
USPTO PCT

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

April 7, 1998

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/050,213

FILING DATE: June 19, 1997

**PRIORITY
DOCUMENT**

**SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)**

**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**



**P. SWAIN
Certifying Officer**

65373 U.S. PTO
06/19/97

PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(h)(2).

Approved

Docket Number	97-038	Type a plus sign (+) inside this box ->	+
---------------	--------	---	---

INVENTOR(S)/APPLICANT(S)

LAST NAME Yang Keating	FIRST NAME Shijun Paul	M.I. J.	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY) 1803 Perrin Court, Maple Glen, PA 19002 2727 Avenue "A" Newportville, PA 19056
------------------------------	------------------------------	------------	--

66052 U.S. PTO
60/050213
06/19/97

TITLE OF INVENTION (280 CHARACTERS MAX)

Plastic Compositions Having Mineral-Like Appearance

CORRESPONDENCE ADDRESS

ROHM AND HAAS COMPANY
100 Independence Mall West
Philadelphia, PA 19106-2399

ATTENTION: T.J. Howell

STATE	PA	ZIP CODE	19106-2399	COUNTRY	UNITED STATES OF AMERICA
-------	----	----------	------------	---------	--------------------------

ENCLOSED APPLICATIONS (Check all that apply)

<input checked="" type="checkbox"/> SPECIFICATION	Number of Pages <u>25</u>	<input type="checkbox"/> Small Entity Statement
<input type="checkbox"/> DRAWING(S)	Number of Sheets <u> </u>	<input type="checkbox"/> Other (Specify) _____
METHOD OF PAYMENT (Check all that apply)		
<input type="checkbox"/> A check or money order is enclosed to cover the Provisional filing fees		PROVISIONAL FILING FEE AMOUNT (\$)
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number: <u>18-1850</u>		<u>\$150.00</u>

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

DO No.

Respectfully submitted,

SIGNATURE Thomas Howell

DATE: June 18, 1997

TYPED or PRINTED NAME Thomas J. Howell

REGISTRATION NO.: 34,351

Additional inventors are being named on separately numbered sheets attached hereto.

PROVISIONAL APPLICATION FILING ONLY

Express Mail Label No. EG367962560U.S.

PATENT APPLICATION OF

Shijun Yang
Paul Joseph Keating

for

PLASTIC COMPOSITIONS HAVING MINERAL-LIKE APPEARANCE

DN 97-038

TJH/EP

PLASTIC COMPOSITIONS HAVING MINERAL-LIKE APPEARANCE

BACKGROUND

5 This invention relates to composite plastic compositions useful in the preparation of simulated natural substances, such as stone-like and mineral-like materials. In particular the present invention involves the use of specific crosslinked polymers together with certain thermoplastic matrices to provide composite plastic compositions having a mineral-like appearance, especially an
10 appearance similar to that of granite.

15 There currently exists a need for synthetic materials that mimic the appearance of mineral-like or ceramic-like materials, such as natural stone, and in particular granite, for use in the manufacture of flooring, tiles, counter tops, sinks, spas, sanitaryware, architectural articles and other ornamental materials. For example, acrylic "granite" sheet products useful in spas, sanitaryware and outdoor applications are currently prepared by cell or continuous casting processes where small granulates are suspended in monomer or monomer/polymer mixtures and then "cured," such as is described in U.S. Patent No. 5,304,592 and WO 97/14749. These thermoset materials can not be further
20 fabricated by conventional thermoplastic processing methods (such as sheet
extrusion and injection molding operations), [REDACTED]
25 processes currently require special handling steps or raw material limitations to uniformly suspend the granulates in the polymerizing matrix during the "cure" step. Reuse and recycling of waste and off-grade materials, such as trimmings, from prior art sheet materials is impractical due to the inherent intractability of
30 the thermoset materials. Prior art "granite" sheet products prepared by casting methods generally have poor impact strength, for example brittleness, and are limited in their adaptability to various formulation or processing methods for producing final articles. In addition, the prior art materials often provide poor adhesion to substrate surfaces resulting in subsequent "delamination" of composite articles.

It is, therefore, desirable to be able to provide thermoplastic materials that may be fabricated by conventional thermoplastic equipment (such as

extrusion or injection molding) for use in spas and outdoor architectural applications; there is a need for an economical and efficient method for reuse and recycling of waste materials that is not available with current thermoset casting processes.

5 The problem addressed by the present invention is to overcome the deficiencies of prior methods used to prepare mineral-like plastics by providing materials that are processable by less labor intensive methods, such as coextrusion or extrusion, while also improving the economics of the processing by allowing for reuse and recycling of waste materials.

10 **STATEMENT OF INVENTION**

The present invention provides a composite plastic composition comprising a particulate crosslinked polymer dispersed within a thermoplastic matrix, wherein (a) the composite plastic composition is comprised of 10 to 45 weight percent of the crosslinked polymer, based on weight of the composite plastic composition, and the crosslinked polymer has a particle size substantially from 0.2 to 1.2 millimeters; (b) the crosslinked polymer is comprised of 0.1 to 15 weight percent inert filler and 0.1 to 20 weight percent crosslinker, based on total weight of crosslinked polymer; and (c) the crosslinked polymer is visually differentiable from the thermoplastic matrix.

20 The present invention further provides a process for preparing a composite plastic composition comprising (a) preparing a crosslinked polymer comprising 0.1 to 15 weight percent inert filler and 0.1 to 20 weight percent crosslinker, based on weight of crosslinked polymer; (b) comminuting the crosslinked polymer to particles having a particle size substantially from 0.2 to 1.2 millimeters; (c) dispersing 10 to 45 weight percent of the particles of crosslinked polymer within 55 to 90 weight percent of a thermoplastic matrix by a heat processing treatment; and (d) recovering the composite plastic composition as a particulate material.

25 In another aspect, the present invention provides a composite plastic composition comprising a particulate crosslinked polymer dispersed within a thermoplastic matrix, wherein (a) the composite plastic composition is comprised of greater than 20 to 40 weight percent of the crosslinked polymer, based on

weight of the composite plastic composition, and the particle size of the crosslinked polymer is substantially from 0.3 to 1.2 millimeters; (b) the crosslinked polymer is comprised of (i) from 95 to 99.5 weight percent (meth)acrylic monomer units selected from one or more of methyl methacrylate, 5 ethyl acrylate and acrylic acid; (ii) from 0.5 to 5 weight percent crosslinker units selected from one or more of allyl methacrylate, ethylene glycol dimethacrylate and divinylbenzene; and (iii) from 0.3 to 5 weight percent inert filler selected from one or more of titanium dioxide, iron oxide, alumina, carbon black, 10 pigments and silica, based on total weight of crosslinked polymer; (c) the thermoplastic matrix is comprised of (i) 50 to 60 weight percent poly(alkyl (meth)acrylate) comprising a copolymer of 80 to 99 weight percent methyl methacrylate monomer units and 1 to 20 weight percent (C₁-C₁₀)alkyl acrylate monomer units, based on weight of poly(alkyl (meth)acrylate); and (ii) 40 to 50 weight percent impact modifier comprising a multi-stage sequentially produced 15 polymer, based on weight of thermoplastic matrix; and (d) the crosslinked polymer is visually differentiable from the thermoplastic matrix.

In other embodiments, the present invention provides a plastic composite composition prepared according to the process described above and an article of manufacture comprising an extruded sheet material resulting from extrusion of
20 the composite plastic composition described above.

DETAILED DESCRIPTION

The process of the present invention is useful for preparing a range of composite plastic compositions suitable for use in forming simulated mineral-like articles. Common to each of the composite compositions is the dispersion of a 25 particulate crosslinked polymer within a thermoplastic matrix. We have found that composite plastic compositions based on selected crosslinked polymers, having selected crosslinking levels and a selected particle size range, result in unexpectedly improved extrusion process performance and the ability to provide "granite-like" plastic articles as compared with prior art plastics using cell-casting processes.

As used herein, the term "thermoplastic" refers to polymers that are reversibly deformable (able to be softened) after being heated above their

softening or glass transition temperatures and then cooled; these materials are capable of being repeatedly melt processed in plastic manufacturing machinery such as, for example, injection molding, extrusion, blow molding, compression molding and rotational molding. As is generally accepted by those skilled in the art, thermoplastic polymers include, for example, acrylonitrile/butadiene/styrene (ABS) terpolymer, acrylonitrile/styrene/acrylate (ASA) copolymer, polycarbonate, polyester, methyl methacrylate/butadiene/styrene (MBS) copolymer, high impact polystyrene (HIPS), acrylonitrile/acrylate copolymer, acrylonitrile/methyl methacrylate copolymer, impact modified polyolefins, impact modified polyvinyl chloride (PVC) and impact modified polymethacrylates.

As used herein, the term "thermoset" refers to polymers that are irreversibly deformable after they have been prepared in an initial configuration, that is, once the polymer is formed by chemical crosslinking (usually thermally induced) it is no longer amenable to thermal processing into other physical forms. As is generally accepted by those skilled in the art, thermoset polymers are polymers that include crosslinking as part of their preparation or have been subjected to crosslinking reactions as part of a post-treatment step, for example, allyl ester polymers, epoxy resins, crosslinked acrylic polymers and crosslinked styrenic polymers produced by suspension, emulsion, continuous-cast or cell-cast polymerization methods.

As used herein, the term "thermoforming" refers to the processing of polymers into 3-dimensional molded forms from flat plastic preformed materials, such as film or sheet, under the influence of heat, pressure or vacuum or combinations thereof.

As used herein, the term "particulate material" refers to any material in the form of separate particles or divided fragments, such as, for example, pellets, beads, powders, granules and chips.

As used herein, the term "alkyl (meth)acrylate" refers to either the corresponding acrylate or methacrylate ester; similarly, the term "(meth)acrylic" refers to either acrylic or methacrylic acid and the corresponding derivatives, such as esters or amides. As used herein, all percentages referred to will be expressed in weight percent (%), based on total weight of polymer or composition

involved, unless specified otherwise. As used herein, the term "copolymer" or "copolymer material" refers to polymer compositions containing units of two or more monomers or monomer types. As used herein, "extrusion blended" and "extrusion compounded" are used synonymously and refer to the intimate mixing 5 of two materials by melt extrusion.

The composite plastic compositions of the present invention use selected crosslinked polymers in combination with selected thermoplastic materials, the latter providing a thermoplastic matrix. Crosslinked polymers useful in the present invention include, for example, crosslinked vinyl polymers (prepared 10 from monoethylenically unsaturated monomers and various multifunctional crosslinking monomers) and crosslinked condensation polymers (such as polyepoxy resins and polyesters, for example, poly(butylene terephthalate) and poly(ethylene terephthalate)). Thermoset polymers represent one class of crosslinked polymers useful in the present invention.

15 Suitable monoethylenically unsaturated monomers useful in preparing particulate crosslinked polymers of the present invention include vinylaromatic monomers, ethylene and substituted ethylene monomers.

Suitable vinylaromatic monomers include, for example, styrene and substituted styrenes, such as α -methylstyrene, vinyltoluene, ortho-, meta- and

The vinylaromatic monomers can also include their substituted counterparts, for example, halogenated derivatives, that is, containing one or more halogen groups (such as fluorine, chlorine and bromine).

Another class of suitable monoethylenically unsaturated monomers is 25 ethylene and substituted ethylene monomers, for example: α -olefins such as propylene, isobutylene and long chain alkyl α -olefins (such as (C₁₀-C₂₀)alkyl α -olefins); vinyl alcohol esters such as vinyl acetate and vinyl stearate; vinyl halides such as vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, vinylidene fluoride and vinylidene bromide; vinyl nitriles such as acrylonitrile 30 and methacrylonitrile; acrylic acid and methacrylic acid and derivatives such as corresponding amides and esters; maleic acid and derivatives such as corresponding anhydride, amides and esters; fumaric acid and derivatives such

as corresponding amides and esters; itaconic and citraconic acids and derivatives such as corresponding anhydrides, amides and esters.

A preferred class of monomers useful in preparing the crosslinked polymers of the present invention are (meth)acrylic monomers, particularly (C₁-C₂₂)alkyl (meth)acrylate monomers. Examples of the alkyl (meth)acrylate monomer where the alkyl group contains from 1 to 6 carbon atoms are methyl methacrylate (MMA), methyl acrylate and ethyl acrylate (EA), propyl methacrylate, butyl methacrylate (BMA), butyl acrylate (BA), isobutyl methacrylate (IBMA), hexyl and cyclohexyl methacrylate, cyclohexyl acrylate and combinations thereof.

Examples of alkyl (meth)acrylate monomers where the alkyl group contains from 7 to 22 carbon atoms are 2-ethylhexyl acrylate (EHA), 2-ethylhexyl methacrylate, octyl methacrylate, decyl methacrylate, isodecyl methacrylate (IDMA, based on branched (C₁₀)alkyl isomer mixture), undecyl methacrylate, dodecyl methacrylate (also known as lauryl methacrylate), tridecyl methacrylate, tetradecyl methacrylate (also known as myristyl methacrylate), pentadecyl methacrylate and combinations thereof. Also useful are: dodecyl-pentadecyl methacrylate (DPMA), a mixture of linear and branched isomers of dodecyl, tridecyl, tetradecyl and pentadecyl methacrylates; and lauryl-myristyl methacrylate (LMA), a mixture of dodecyl and tetradecyl methacrylates.

Additional (C₇-C₂₂)alkyl (meth)acrylate monomers include hexadecyl methacrylate (also known as cetyl methacrylate), heptadecyl methacrylate, octadecyl methacrylate (also known as stearyl methacrylate), nonadecyl methacrylate, eicosyl methacrylate, behenyl methacrylate and combinations thereof; also useful are cetyl-eicosyl methacrylate (CEMA), a mixture of hexadecyl, octadecyl, and eicosyl methacrylate; and cetyl-stearyl methacrylate (SMA), a mixture of hexadecyl and octadecyl methacrylate.

Suitable crosslinking monomers include, for example, ethylene glycol dimethacrylate, polyethylene glycol diacrylate and dimethacrylate, propylene glycol dimethacrylate and diacrylate, glycidyl methacrylate, divinylbenzene, triallyl isocyanurate, N-(hydroxymethyl)acrylamide, allyl acrylate, allyl

methacrylate, N,N'-methylene diacrylamide and dimethacrylamide, triallyl citrate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, and diethyleneglycol divinyl ether. Preferred crosslinkers are allyl methacrylate, ethylene glycol dimethacrylate and divinylbenzene. The amount of crosslinking monomer is generally from 0.1 to 20%, typically from 0.5 to 10%, preferably from 0.5 to 5%, more preferably from 1 to 4% and most preferably from greater than 1.5% to 3%, based on total weight of the crosslinked polymer, that is, combined weight of monoethylenically unsaturated monomer and the crosslinking monomer.

Suitable free-radical initiators useful in the present invention are any of the well known free-radical-producing compounds such as peroxy and hydroperoxy initiators, including, for example, acetyl peroxide, benzoyl peroxide, lauroyl peroxide, caproyl peroxide, cumene hydroperoxide, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, tert-butyl peroxyisobutyrate, tert-butyl peracetate, tert-butyl peroxy-pivalate (TBPV) and tert-butyl peroxyoctoate (TBP, also known as tert-butylperoxy-2-ethylhexanoate). Also useful, for example, are azo initiators such as azodiisobutyronitrile (AIBN), azodiisobutyramide, 2,2'-azobis(2,4-dimethylvaleronitrile), azo-bis(α -methylbutyronitrile) and dimethyl-, diethyl- or dibutyl azo-bis(methylvalerate). The initiator concentration is

from 0.1 to 1%, by weight based on the total weight of the monomers. In addition to the initiator, one or more promoters may also be used; preferably the promoters are hydrocarbon-soluble. Alternatively, little or no free-radical initiator may be used and the polymerization is then thermally induced by heating the monomer mixture.

The crosslinked polymer also contains inert filler that may be conveniently added to a cell casting syrup before starting the polymerization. Suitable inert fillers, include, for example, alumina (including hydrated forms), titanium dioxide, zinc oxide, zinc sulfide, iron oxide, barium sulfate, zirconium silicate, strontium sulfate, calcium carbonate, carbon black, powdered glass, silica, clay and talc. Preferred inert fillers include titanium dioxide, iron oxide, carbon black, silica, alumina, pigments and combinations thereof; most preferred

is titanium dioxide. Conventional pigments or colorants include organic dyes (for example azo, anthraquinone, perinone, quinoline, pyrazolone, dioxazine, isoindoline, phthalocyanine, quinacridone and coumarin derivatives) and inorganic salts (cadmium, chromates, iron blue, cobalt blue and ultramarine blue). Typically, the amount of inert filler is from 0.1 to 15%, preferably from 0.2 to 10% and more preferably from 0.3 to 5%, based on total weight of crosslinked polymer. The purpose of the inert filler is to enhance the visual differentiation between the crosslinked polymer component and the thermoplastic matrix component to provide the "mineral-like" or "granite-like" appearance of the finished composite plastic composition.

Optionally, the crosslinked polymer may contain conventional adjuvants, known to those skilled in the art, for various purposes, for example: dyes, pigments, antioxidants, ultraviolet stabilizers, dispersants, processing aids (such as spray drying aids, lubricants and mold-release agents), flame retardants, polymerization rate-moderators and viscosity controlling materials. In addition, these same conventional adjuvants may be conveniently added at later stages in the production of the composite plastic composition, for example, during preparation of the thermoplastic material used as the thermoplastic matrix (described below) or during the production of the composite plastic composition itself where the crosslinked polymer and thermoplastic material are extrusion blended or compounded.

Typically, the particulate crosslinked polymers of the present invention are selected from the group consisting of crosslinked poly(alkyl (meth)acrylate), crosslinked poly(vinylaromatic), crosslinked polyester, crosslinked polyolefin, mixtures and corresponding copolymers thereof. Preferred crosslinked polymers are crosslinked poly(alkyl (meth)acrylates) and crosslinked polystyrene where the crosslinked polymer comprises 90 to 99.5% monomer units selected from one or more of vinylaromatic monomer and (meth)acrylic monomer and 0.5 to 10% crosslinker, based on weight of crosslinked polymer.

The crosslinked polymer material is conveniently prepared by a cell casting process, for example. In a typical cell casting process a monomer syrup containing the monoethylenically unsaturated monomers, a crosslinking agent

and a free-radical initiator is subjected to a temperature suitable for polymerization, depending on the monomers and initiators used. Preferred monoethylenically unsaturated monomers are alkyl (meth)acrylate monomers, for example, (C₁-C₄)alkyl (meth)acrylates, such as MMA (typically 80 to 99.5% and preferably from 95 to 99.5%, based on total weight of monomers), methylacrylate or EA (typically from zero to 20%, preferably from 1 to 8% and more preferably from 0.5 to 5%, based on total weight of monomers), propyl methacrylate, BMA, BA, IBMA and combinations thereof. Optionally, acrylic or methacrylic acid may be included, typically from zero 2%, based on total weight of monomers.

After the crosslinked polymer is prepared, such as by cell cast polymerization, it is comminuted to a particulate material by known processes, for example, chipping, crushing, grinding, shredding or any granulation method; if suspension or emulsion polymerization processes are used to prepare the crosslinked polymer, conventional isolation processes used to recover the crosslinked polymer in particulate form include, for example filtration, coagulation and spray drying. The dimensions of the particulate crosslinked polymer are typically from 0.2 to about 1.2 millimeters (mm) or about 16 to 70 U.S. standard mesh. Generally, the particle size of the particulate crosslinked

to 1.2 mm (16 to 50 mesh), more preferably from 0.4 to 1.0 mm (18 to 40 mesh) and most preferably from 0.4 to 0.85 mm (20 to 40 mesh). When the particle size of the crosslinked polymer is smaller than about 70 mesh or larger than about 16 mesh, the extrusion blending of the crosslinked polymer into the thermoplastic matrix becomes problematic, for example "stranding" problems, and the desired "speckle-like" or "mineral-like" effect may not be readily attained in the final decorative or architectural article.

Thermoplastic materials useful to provide the thermoplastic matrix of the present invention include, for example, alkyl (meth)acrylate polymers and copolymers having little or no crosslinker. The thermoplastic materials are conveniently prepared by conventional cell casting or melt extrusion processes and are typically provided in particulate form. In addition, the thermoplastic

materials may be prepared by conventional bulk (for example, continuous flow stirred tank reactor (CFSTR) processes), solution, suspension or emulsion polymerization techniques, in which case conventional isolation processes used to recover the polymer in particulate form include, for example filtration, 5 coagulation and spray drying. Conditions for polymerization of monomers to produce the thermoplastic material are similar to those described above for cell casting polymerization, except that little or no crosslinker is involved; when melt extrusion methods are used, the thermoplastic material is conveniently isolated in a particulate form, such as pellets or granules. Suitable alkyl (meth)acrylate 10 monomers include, for example, the (C₁-C₂₂)alkyl (meth)acrylates monomers described above for the use in preparing the crosslinked polymers. Preferably the thermoplastic matrix material comprises a polymer or copolymer of methyl methacrylate (MMA); typical copolymers include 80 to 99% MMA and 1 to 20%, preferably 1 to 5%, of (C₁-C₁₀)alkyl acrylates, such as methyl acrylate and ethyl 15 acrylate (EA). A suitable commercially available poly(methyl methacrylate) type thermoplastic matrix material is Plexiglas V-grade molding powder, such as Plexiglas VO-825, VO-825HID, VO-45, VO-52 and VO-920.

Additional suitable thermoplastic polymers include, for example, ABS terpolymer, ASA copolymer, polycarbonate, polyester (such as poly(butylene terephthalate) and poly(ethylene terephthalate)), MBS copolymer, HIPS, acrylonitrile/acrylate copolymer, acrylonitrile/methyl methacrylate copolymer, impact modified polyolefins and impact modified PVC. More preferably the thermoplastic matrix material is an impact modified polymethacrylate.

The thermoplastic matrix may be based entirely on the aforementioned 25 thermoplastic polymers or the thermoplastic matrix may optionally contain modifier additives, such as impact modifiers, in addition to the aforementioned thermoplastic polymers. In general, the thermoplastic matrix comprises 50 to 100% poly(alkyl (meth)acrylate) and zero to 50% impact modifier, based on weight of thermoplastic matrix. Typically, the thermoplastic matrix contains 25 to 100%, preferably 30 to 70%, more preferably 45 to 60% and most preferably 50 to 60%, thermoplastic polymer, such as poly(alkyl (meth)acrylate); and zero to 75%, preferably 30 to 70%, more preferably 40 to 55% and most preferably 40 to

50%, impact modifier, based on total weight of thermoplastic matrix. Suitable impact modifiers include, for example, elastomeric polymers such as graft polymers of methyl methacrylate and styrene on butadiene (MBS), graft polymers of acrylonitrile and styrene on butadiene (ABS), copolymers of styrene 5 and butadiene, poly(butyl acrylate) and poly(2-ethylhexyl acrylate) and copolymers thereof, copolymers of butyl acrylate and methyl acrylate, terpolymers of butyl acrylate/styrene/methyl methacrylate, chlorinated polyethylene, acrylate block polymers, styrene block polymers, ethylene/propylene/diene copolymer (EPDM), ethylene/vinyl acetate copolymers, 10 acrylonitrile/styrene/acrylic ester terpolymers, styrene-maleic anhydride copolymers and core-shell multi-stage sequentially-produced polymers. Preferred impact modifiers include MBS polymers, core-shell multi-stage sequentially-produced polymers, and styrene and acrylate block polymers.

Typical core-shell multi-stage polymers useful as impact modifiers for 15 thermoplastic polymers include, for example, those disclosed in U.S. Patent No. 3,793,402. The multi-stage sequentially-produced polymers are characterized by having at least three stages in a sequence of a non-elastomeric first stage, an elastomeric second stage and a non-elastomeric third stage. Preferably the first stage polymer has a glass transition temperature (T_g) greater than about 25°C,

preferably 85 to 99.9%, monomer units of one or more of (C_1 - C_4)alkyl (meth)acrylates (preferably MMA and EA), styrene, substituted styrene, acrylonitrile and methacrylonitrile, based on weight of the first stage polymer; 25 (b) zero to 10%, preferably 0.05 to 5% and more preferably 0.5 to 2%, monomer units of a copolymerizable polyfunctional crosslinking monomer; (c) zero to 10%, preferably 0.05 to 5%, monomer units of a copolymerizable graftlinking monomer, such as the allyl, methallyl and crotyl esters of monoethylenically unsaturated monocarboxylic and dicarboxylic acids, for example allyl methacrylate; and (d) zero to 30%, preferably 0.1 to 15%, of other copolymerizable 30 monoethylenically unsaturated monomers.

The second stage polymer is prepared in the presence of the first stage polymer and preferably has a T_g of less than about 25°C, preferably less than about 10°C, if it were to be prepared alone, that is in the absence of the presence of the first stage polymer. Typically the second stage polymer comprises (a) 50 to 5 99.9%, preferably 70 to 99.5%, monomer units of one or more of (C₁-C₈)alkyl (meth)acrylates, (preferably (C₁-C₄)alkyl acrylates, particularly BA), butadiene and substituted butadienes (such as isoprene, chloroprene and 2,3-dimethylbutadiene), based on weight of the second stage polymer; (b) zero to 10 49.9%, preferably 0.5 to 30%, monomer units of a copolymerizable monoethylenically unsaturated monomer, such as styrene and substituted styrene; (c) zero to 5% monomer units of a copolymerizable polyfunctional crosslinking monomer, such as ethylene glycol diacrylate and divinylbenzene; and (d) 0.05 to 5% monomer units of a copolymerizable graftlinking monomer, such as those described above.

15 The third stage polymer is prepared in the presence of the product of the first and second stage polymers and preferably has a T_g greater than about 25°C, preferably greater than about 50°C, if it were to be prepared alone, that is in the absence of the presence of the product of the first and second stage polymers. Typically the third stage polymer comprises (a) 70 to 100%, preferably 20 85 to 99.9%, monomer units of one or more of (C₁-C₄)alkyl (meth)acrylates, styrene, substituted styrene, acrylonitrile and methacrylonitrile, based on weight of the second stage polymer; (b) zero to 30, preferably 0.1 to 15%, monomer units of a copolymerizable monoethylenically unsaturated monomer; (c) zero to 10%, preferably 0.05 to 5%, monomer units of a copolymerizable 25 polyfunctional crosslinking monomer; and (d) zero to 5% monomer units of a copolymerizable graftlinking monomer, such as those described above.

Typically the multi-stage polymer comprises at least three stages in a sequence of 10 to 40%, preferably 20 to 40%, of the first stage; 20 to 60%, preferably 30 to 50%, of the second stage; and 10 to 70%, preferably 20 to 50%, of 30 the third stage, based on total weight of the multi-stage polymer.

Other copolymerizable mononethylenically unsaturated monomers referred to above include alkyl (meth)acrylates, alkoxy (meth)acrylates, hydroxyalkyl (meth)acrylates, cyanoethyl (meth)acrylates, (meth)acrylamides, (meth)acrylic acids and vinyl aromatics, for example.

5 Typical copolymerizable polyfunctional crosslinking monomers include, for example, ethylene glycol dimethacrylate and diacrylate, 1,3-butylene glycol dimethacrylate and diacrylate, 1,4-butylene glycol dimethacrylate and diacrylate, propylene glycol dimethacrylate, divinylbenzene, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate and diethyleneglycol divinyl
10 ether. Preferred crosslinkers are ethylene glycol dimethacrylate and divinylbenzene. For the purpose of the preparing the multi-stage sequentially-produced polymers, the crosslinkers are selected from polyfunctional monomers where the crosslinking groups have similar reactivities, such as those just described. Polyfunctional "crosslinking" monomers where the functional groups
15 have different reactivities, such as allyl methacrylate and methallyl and crotyl esters of monoethylenically unsaturated monocarboxylic and dicarboxylic acids, are referred to as "graftlinking" monomers when used in preparation of the multi-stage sequentially-produced polymers described herein; however they are considered to be among the general group of "crosslinking" monomers useful in

particulate crosslinked polymers of the present invention.

Preferably, the multi-stage polymer is an emulsion polymer comprising monomer units of methyl methacrylate in the first stage, monomer units selected from one or more of butadiene, styrene and (C₁-C₈)alkyl acrylates in the second
25 stage, and monomer units selected from one or more of (C₁-C₄)alkyl methacrylates, styrene and acrylonitrile in the third stage.

The multi-stage polymers may be prepared by a number of well-known techniques, for example, by emulsion polymerization, where a subsequent stage monomer mixture is polymerized in the presence of a previously formed product.
30 For example, "sequentially produced" or "sequentially polymerized" refer to polymers prepared in aqueous dispersion or emulsion form where successive

monomer charges are polymerized onto or in the presence of a preformed latex prepared by the polymerization of a prior monomer charge and stage.

The blend of the multi-stage polymer (as an impact modifier) with the thermoplastic polymer can be accomplished by any known method, such as dispersing the multi-stage polymer in a monomer mixture used to prepare the thermoplastic polymer or in a monomer-polymer syrup mixture which together would provide the desired thermoplastic polymer. Alternatively, the multi-stage polymer can be placed in a casting mix in the form of an emulsion, suspension or dispersion in water or in an organic carrier; the water or organic carrier can then be removed before or after casting into the final thermoplastic polymer form. The multi-stage polymer may also be blended with the thermoplastic polymer by extrusion compounding. Additional specific methods and details of blending the thermoplastic polymer and impact modifiers are disclosed in U.S. Patent No. 3,793,402.

A preferred thermoplastic matrix material is impact modified poly(methyl methacrylate) commercially available as Plexiglas DR101, MI-5 and MI-7 molding powder. Plexiglas (North and South America, Oroglass in Europe and Asia) is a trademark of Rohm and Haas Company, Philadelphia, PA, USA.

In one embodiment of the present invention, the composite plastic compositions of the present invention are prepared by compounding or blending the crosslinked polymer with the thermoplastic material by dispersing particles of crosslinked polymer within a matrix of thermoplastic material using a suitable heat processing treatment. Suitable heat processing treatments include, for example, extrusion blending, hot-melt kneading and hot-melt batch mixing. For example, the crosslinked polymer particles may be melt processed by hot melt extrusion blending or compounding with thermoplastic particles and the resultant composite plastic composition is recovered in particulate form, such as pellets. Hot-melt batch mixing may include dispersion of the crosslinked particles into a melt of the thermoplastic matrix in a conventional batch mode, such as a stirred kettle; alternatively, the thermoplastic may be heated and mixed with a carrier solvent, such as toluene, and then batch mixed with the crosslinked particles, followed by flash evaporation of the solvent; the resultant

15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200
205
210
215
220
225
230
235
240
245
250
255
260
265
270
275
280
285
290
295
300
305
310
315
320
325
330
335
340
345
350
355
360
365
370
375
380
385
390
395
400
405
410
415
420
425
430
435
440
445
450
455
460
465
470
475
480
485
490
495
500
505
510
515
520
525
530
535
540
545
550
555
560
565
570
575
580
585
590
595
600
605
610
615
620
625
630
635
640
645
650
655
660
665
670
675
680
685
690
695
700
705
710
715
720
725
730
735
740
745
750
755
760
765
770
775
780
785
790
795
800
805
810
815
820
825
830
835
840
845
850
855
860
865
870
875
880
885
890
895
900
905
910
915
920
925
930
935
940
945
950
955
960
965
970
975
980
985
990
995
1000
1005
1010
1015
1020
1025
1030
1035
1040
1045
1050
1055
1060
1065
1070
1075
1080
1085
1090
1095
1100
1105
1110
1115
1120
1125
1130
1135
1140
1145
1150
1155
1160
1165
1170
1175
1180
1185
1190
1195
1200
1205
1210
1215
1220
1225
1230
1235
1240
1245
1250
1255
1260
1265
1270
1275
1280
1285
1290
1295
1300
1305
1310
1315
1320
1325
1330
1335
1340
1345
1350
1355
1360
1365
1370
1375
1380
1385
1390
1395
1400
1405
1410
1415
1420
1425
1430
1435
1440
1445
1450
1455
1460
1465
1470
1475
1480
1485
1490
1495
1500
1505
1510
1515
1520
1525
1530
1535
1540
1545
1550
1555
1560
1565
1570
1575
1580
1585
1590
1595
1600
1605
1610
1615
1620
1625
1630
1635
1640
1645
1650
1655
1660
1665
1670
1675
1680
1685
1690
1695
1700
1705
1710
1715
1720
1725
1730
1735
1740
1745
1750
1755
1760
1765
1770
1775
1780
1785
1790
1795
1800
1805
1810
1815
1820
1825
1830
1835
1840
1845
1850
1855
1860
1865
1870
1875
1880
1885
1890
1895
1900
1905
1910
1915
1920
1925
1930
1935
1940
1945
1950
1955
1960
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
2020
2025
2030
2035
2040
2045
2050
2055
2060
2065
2070
2075
2080
2085
2090
2095
2100
2105
2110
2115
2120
2125
2130
2135
2140
2145
2150
2155
2160
2165
2170
2175
2180
2185
2190
2195
2200
2205
2210
2215
2220
2225
2230
2235
2240
2245
2250
2255
2260
2265
2270
2275
2280
2285
2290
2295
2300
2305
2310
2315
2320
2325
2330
2335
2340
2345
2350
2355
2360
2365
2370
2375
2380
2385
2390
2395
2400
2405
2410
2415
2420
2425
2430
2435
2440
2445
2450
2455
2460
2465
2470
2475
2480
2485
2490
2495
2500
2505
2510
2515
2520
2525
2530
2535
2540
2545
2550
2555
2560
2565
2570
2575
2580
2585
2590
2595
2600
2605
2610
2615
2620
2625
2630
2635
2640
2645
2650
2655
2660
2665
2670
2675
2680
2685
2690
2695
2700
2705
2710
2715
2720
2725
2730
2735
2740
2745
2750
2755
2760
2765
2770
2775
2780
2785
2790
2795
2800
2805
2810
2815
2820
2825
2830
2835
2840
2845
2850
2855
2860
2865
2870
2875
2880
2885
2890
2895
2900
2905
2910
2915
2920
2925
2930
2935
2940
2945
2950
2955
2960
2965
2970
2975
2980
2985
2990
2995
3000
3005
3010
3015
3020
3025
3030
3035
3040
3045
3050
3055
3060
3065
3070
3075
3080
3085
3090
3095
3100
3105
3110
3115
3120
3125
3130
3135
3140
3145
3150
3155
3160
3165
3170
3175
3180
3185
3190
3195
3200
3205
3210
3215
3220
3225
3230
3235
3240
3245
3250
3255
3260
3265
3270
3275
3280
3285
3290
3295
3300
3305
3310
3315
3320
3325
3330
3335
3340
3345
3350
3355
3360
3365
3370
3375
3380
3385
3390
3395
3400
3405
3410
3415
3420
3425
3430
3435
3440
3445
3450
3455
3460
3465
3470
3475
3480
3485
3490
3495
3500
3505
3510
3515
3520
3525
3530
3535
3540
3545
3550
3555
3560
3565
3570
3575
3580
3585
3590
3595
3600
3605
3610
3615
3620
3625
3630
3635
3640
3645
3650
3655
3660
3665
3670
3675
3680
3685
3690
3695
3700
3705
3710
3715
3720
3725
3730
3735
3740
3745
3750
3755
3760
3765
3770
3775
3780
3785
3790
3795
3800
3805
3810
3815
3820
3825
3830
3835
3840
3845
3850
3855
3860
3865
3870
3875
3880
3885
3890
3895
3900
3905
3910
3915
3920
3925
3930
3935
3940
3945
3950
3955
3960
3965
3970
3975
3980
3985
3990
3995
4000
4005
4010
4015
4020
4025
4030
4035
4040
4045
4050
4055
4060
4065
4070
4075
4080
4085
4090
4095
4100
4105
4110
4115
4120
4125
4130
4135
4140
4145
4150
4155
4160
4165
4170
4175
4180
4185
4190
4195
4200
4205
4210
4215
4220
4225
4230
4235
4240
4245
4250
4255
4260
4265
4270
4275
4280
4285
4290
4295
4300
4305
4310
4315
4320
4325
4330
4335
4340
4345
4350
4355
4360
4365
4370
4375
4380
4385
4390
4395
4400
4405
4410
4415
4420
4425
4430
4435
4440
4445
4450
4455
4460
4465
4470
4475
4480
4485
4490
4495
4500
4505
4510
4515
4520
4525
4530
4535
4540
4545
4550
4555
4560
4565
4570
4575
4580
4585
4590
4595
4600
4605
4610
4615
4620
4625
4630
4635
4640
4645
4650
4655
4660
4665
4670
4675
4680
4685
4690
4695
4700
4705
4710
4715
4720
4725
4730
4735
4740
4745
4750
4755
4760
4765
4770
4775
4780
4785
4790
4795
4800
4805
4810
4815
4820
4825
4830
4835
4840
4845
4850
4855
4860
4865
4870
4875
4880
4885
4890
4895
4900
4905
4910
4915
4920
4925
4930
4935
4940
4945
4950
4955
4960
4965
4970
4975
4980
4985
4990
4995
5000
5005
5010
5015
5020
5025
5030
5035
5040
5045
5050
5055
5060
5065
5070
5075
5080
5085
5090
5095
5100
5105
5110
5115
5120
5125
5130
5135
5140
5145
5150
5155
5160
5165
5170
5175
5180
5185
5190
5195
5200
5205
5210
5215
5220
5225
5230
5235
5240
5245
5250
5255
5260
5265
5270
5275
5280
5285
5290
5295
5300
5305
5310
5315
5320
5325
5330
5335
5340
5345
5350
5355
5360
5365
5370
5375
5380
5385
5390
5395
5400
5405
5410
5415
5420
5425
5430
5435
5440
5445
5450
5455
5460
5465
5470
5475
5480
5485
5490
5495
5500
5505
5510
5515
5520
5525
5530
5535
5540
5545
5550
5555
5560
5565
5570
5575
5580
5585
5590
5595
5600
5605
5610
5615
5620
5625
5630
5635
5640
5645
5650
5655
5660
5665
5670
5675
5680
5685
5690
5695
5700
5705
5710
5715
5720
5725
5730
5735
5740
5745
5750
5755
5760
5765
5770
5775
5780
5785
5790
5795
5800
5805
5810
5815
5820
5825
5830
5835
5840
5845
5850
5855
5860
5865
5870
5875
5880
5885
5890
5895
5900
5905
5910
5915
5920
5925
5930
5935
5940
5945
5950
5955
5960
5965
5970
5975
5980
5985
5990
5995
6000
6005
6010
6015
6020
6025
6030
6035
6040
6045
6050
6055
6060
6065
6070
6075
6080
6085
6090
6095
6100
6105
6110
6115
6120
6125
6130
6135
6140
6145
6150
6155
6160
6165
6170
6175
6180
6185
6190
6195
6200
6205
6210
6215
6220
6225
6230
6235
6240
6245
6250
6255
6260
6265
6270
6275
6280
6285
6290
6295
6300
6305
6310
6315
6320
6325
6330
6335
6340
6345
6350
6355
6360
6365
6370
6375
6380
6385
6390
6395
6400
6405
6410
6415
6420
6425
6430
6435
6440
6445
6450
6455
6460
6465
6470
6475
6480
6485
6490
6495
6500
6505
6510
6515
6520
6525
6530
6535
6540
6545
6550
6555
6560
6565
6570
6575
6580
6585
6590
6595
6600
6605
6610
6615
6620
6625
6630
6635
6640
6645
6650
6655
6660
6665
6670
6675
6680
6685
6690
6695
6700
6705
6710
6715
6720
6725
6730
6735
6740
6745
6750
6755
6760
6765
6770
6775
6780
6785
6790
6795
6800
6805
6810
6815
6820
6825
6830
6835
6840
6845
6850
6855
6860
6865
6870
6875
6880
6885
6890
6895
6900
6905
6910
6915
6920
6925
6930
6935
6940
6945
6950
6955
6960
6965
6970
6975
6980
6985
6990
6995
7000
7005
7010
7015
7020
7025
7030
7035
7040
7045
7050
7055
7060
7065
7070
7075
7080
7085
7090
7095
7100
7105
7110
7115
7120
7125
7130
7135
7140
7145
7150
7155
7160
7165
7170
7175
7180
7185
7190
7195
7200
7205
7210
7215
7220
7225
7230
7235
7240
7245
7250
7255
7260
7265
7270
7275
7280
7285
7290
7295
7300
7305
7310
7315
7320
7325
7330
7335
7340
7345
7350
7355
7360
7365
7370
7375
7380
7385
7390
7395
7400
7405
7410
7415
7420
7425
7430
7435
7440
7445
7450
7455
7460
7465
7470
7475
7480
7485
7490
7495
7500
7505
7510
7515
7520
7525
7530
7535
7540
7545
7550
7555
7560
7565
7570
7575
7580
7585
7590
7595
7600
7605
7610
7615
7620
7625
7630
7635
7640
7645
7650
7655
7660
7665
7670
7675
7680
7685
7690
7695
7700
7705
7710
7715
7720
7725
7730
7735
7740
7745
7750
7755
7760
7765
7770
7775
7780
7785
7790
7795
7800
7805
7810
7815
7820
7825
7830
7835
7840
7845
7850
7855
7860
7865
7870
7875
7880
7885
7890
7895
7900
7905
7910
7915
7920
7925
7930
7935
7940
7945
7950
7955
7960
7965
7970
7975
7980
7985
7990
7995
8000
8005
8010
8015
8020
8025
8030
8035
8040
8045
8050
8055
8060
8065
8070
8075
8080
8085
8090
8095
8100
8105
8110
8115
8120
8125
8130
8135
8140
8145
8150
8155
8160
8165
8170
8175
8180
8185
8190
8195
8200
8205
8210
8215
8220
8225
8230
8235
8240
8245
8250
8255
8260
8265
8270
8275
8280
8285
8290
8295
8300
8305
8310
8315
8320
8325
8330
8335
8340
8345
8350
8355
8360
8365
8370
8375
8380
8385
8390
8395
8400
8405
8410
8415
8420
8425
8430
8435
8440
8445
8450
8455
8460
8465
8470
8475
8480
8485
8490
8495
8500
8505
8510
8515
8520
8525
8530
8535
8540
8545
8550
8555
8560
8565
8570
8575
8580
8585
8590
8595
8600
8605
8610
8615
8620
8625
8630
8635
8640
8645
8650
8655
8660
8665
8670
8675
8680
8685
8690
8695
8700
8705
8710
8715
8720
8725
8730
8735
8740
8745
8750
8755
8760
8765
8770
8775
8780
8785
8790
8795
8800
8805
8810
8815
8820
8825
8830
8835
8840
8845
8850
8855
8860
8865
8870
8875
8880
8885
8890
8895
8900
8905
8910
8915
8920
8925
8930
8935
8940
8945
8950
8955
8960
8965
8970
8975
8980
8985
8990
8995
9000
9005
9010
9015
9020
9025
9030
9035
9040
9045
9050
9055
9060
9065
9070
9075
9080
9085
9090
9095
9100
9105
9110
9115
9120
9125
91

composite plastic composition can then be granulated by conventional means. The resultant pellets are typically translucent to clear granules containing distinct "speckle-like" particles, the latter being representative of the crosslinked polymer used in the compounding process.

5 Typically 10 to 45%, preferably 15 to 40% and more preferably greater than 20 to 40%, crosslinked polymer particles are combined with 55 to 90%, preferably from 60 to 85% and more preferably from 60 to less than 80%, thermoplastic particles, based on combined weight of crosslinked polymer and thermoplastic particles. The extrusion blending process allows for a relatively
10 uniform distribution of the thermoset material throughout the thermoplastic matrix without requiring similar densities of the two materials, as is typically required in conventional casting processes used in the prior art. Preferably a low-shear screw design is used to minimize processing problems, such as residual monomer odor, vent plugging, flowability problems and stranding
15 problems.

Extrusion temperatures are typically in the range of 220° to 260°C and the extruder screw design should provide low shear to prevent the loss of the distinct granite-like appearance and to maintain particle integrity. The cooling bath temperature (strand takeup) is typically maintained at about 60° to 70°C
20 and the various processing problems.

During the extrusion blending process, control of the particle size of crosslinked polymer is important for optimum processing and ultimate "granite-like" appearance of the finished articles. When the particles are very large, that
25 is, greater than about 1.2 mm or 16 mesh, "stranding" problems may develop during sheet extrusion or extrusion blending processes. When the particles are much smaller than about 0.2 mm or 70 mesh, the extruder die may plug frequently and stranding problems may develop; in addition, poor "granite-like" appearance occurs.

30 If the crosslinking level is too low, that is, below about 0.5%, the crosslinked polymer particles may "smear" into thermoplastic matrix material after multiple passes during extrusion, resulting in blurred or non-differentiated

mineral-like appearance. If the crosslinking level is too high, that is, above about 10%, the yield of desired particle size during the comminution step is reduced due to generation of fine particles smaller than about 0.2 mm (70 mesh) and the sheet surfaces of the final article may be rough and require a secondary 5 treatment such as press polishing. Preferably, the crosslinker level is from 0.5 to 5% and more preferably from 1 to 4%.

An example of the importance of the degree of crosslinking in the particulate material regarding the maintenance of particle integrity during processing can be seen in the multiple extrusion processes typically involved in 10 preparing monolithic and multilayed composite sheets. When prior art particles ("C" particles from Safas Corp., mixture of thermoplastic and thermoset material - see Example 3E-3G) were extrusion blended with thermoplastic matrix material at a low concentration (less than 10%), the final sheet provided a hazy speckle-like appearance (not "granite-like"). At a 25% use rate, about half of the 15 "C" particles were smeared into thermoplastic matrix resulting in a non-differentiated final product appearance. When the use rate of "C" particles was above 30%, extrusion process problems were observed (power surges, poor flow, stranding problem, extruder pluggage) as well as complete loss of granite-like effect in the composite plastic material. Composite plastic compositions prepared using the "C" particles discussed above (thermoset/thermoplastic particles disclosed in U.S. Patent No 5,304,592) undergo loss of granite-like 20 appearance under the extrusion processing conditions described in Example 3, apparently due to insufficient particle integrity.

Simulated mineral articles are prepared from the composite plastic 25 compositions of the present invention by heat treatment into a physical form selected from the group consisting of sheet, laminated sheet and molded material. Suitable heat treatment processes include, for example, melt extrusion, coextrusion, blow molding, sheet forming and thermoforming.

The composite plastic compositions of the present invention can be 30 extruded into monolithic sheet for indoor or outdoor applications, or coextruded with other high-impact grade thermoplastics such as ABS terpolymer, ASA copolymer, polycarbonate, MBS copolymer, HIPS, acrylonitrile/acrylate

copolymer, acrylonitrile/methyl methacrylate copolymer, impact modified polyolefins and impact modified PVC, to produce a multilayer composite sheet useful for spa, sanitary ware, countertops, bathroom and kitchen fixtures, wall decorations and other thermoforming applications. The composite plastic 5 compositions may also be injection molded into different forms for other applications such as facets, frames, door handles, window frames, sinks, shower stalls, building panels, plumbing fixtures, tiles, refrigerator walls, floor coverings and decorative moldings.

Some embodiments of the invention are described in detail in the 10 following Examples. All ratios, parts and percentages are expressed by weight unless otherwise specified, and all reagents used are of good commercial quality unless otherwise specified. Abbreviations used in the Examples and Tables are listed below with the corresponding descriptions.

MMA	=	Methyl Methacrylate
EA	=	Ethyl Acrylate
AA	=	Acrylic Acid
ALMA	=	Allyl Methacrylate
AIBN	=	Azodiisobutyronitrile
TBP	=	tert-Butyl Peroctoate
TBPV	=	tert-Butyl Peroxypivalate
		Titanium Dioxide

15

Example 1 Preparation of Crosslinked Polymer

A monomer mixture was prepared by combining crosslinker monomer (ALMA), alkyl (meth)acrylate monomer (MMA), (meth)acrylic comonomer (EA, AA), inert filler (TiO_2 , silica, carbon black), free-radical initiator (AIBN, TBP, 20 TBPV mixture, 0.05%) polymerization rate-moderator (terpinolene, 0.01%) and lubricant (2% stearic acid). All % values are by weight based on total weight of monomers.

The ingredients listed above (monomer mixture) were mixed in a glass casting cell or polyvinyl alcohol (PVA) casting bag and then subjected to a 25 controlled temperature of 60°C for 14 hours, followed by a post-cure (heating at 130°C for 2 hours). The finished crosslinked polymer was recovered by

disassembly of the cell or removal of the PVA bag and was then granulated into particulate form using any conventional grinding method, for example, crushing, attrition mill or Cumberland cutter. The granulated crosslinked polymer was then screened to a desired particle size distribution.

5 Table I summarizes crosslinked polymers (component % based on weight of crosslinked polymer, monomers plus crosslinker) evaluated in the composite plastic compositions of the present invention. Crosslinked polymers typically contained less than 1% residual monomer and were screened after comminution to particulate form, with a typical isolated yield of 65 to 80% particles of -18+40
10 U.S. standard mesh (0.4 mm to 1 mm).

Table I
Compositions of Crosslinked Polymers

ID	Monomers ^a	Crosslinker ^b	Inert Filler ^c
1A	94.5/3.1/2.1	0.3	3
1B	93.0/3.0/2.0	2.0	3
1C	93.0/3.1/0.0	3.9	3
1D	95.0/3.1/0.0	1.9	2/2 ^d
1E ^e	96/4/0	0.0	2.6

a = MMA/EA/AA

b = ALMA

c = Titanium Dioxide

d = Silica/Carbon Black

e = Uncrosslinked. weight average molecular weight approx 3×10^6

20 **Example 2** Preparation of Thermoplastic Matrix Material

The thermoplastic matrix material used in evaluating the composite plastic compositions of the present invention was impact modified poly(methyl methacrylate) commercially available as Plexiglas DR101 molding powder from Rohm and Haas Co, Philadelphia, PA, USA.

25 **Example 3** Preparation of Composite Plastic Composition

The particulate crosslinked polymer (0.4 to 1 mm granules) of Example 1 were extrusion blended (using a single- or twin-screw extruder at 220 to 260°C) with the thermoplastic material (pellets of approximately 3 to 6 mm in diameter and length) of Example 2 (in the relative amounts indicated) into the composite
30 plastic composition of the present invention (see Table 2). The pelletized composite plastic compositions were then sheet extruded and evaluated for their

aesthetic and processing characteristics. Examples 3A-3D represent the present invention and 3E-3G represent comparative examples that replace the particulate crosslinked polymer of the present invention with thermoplastic/thermoset particles based on U.S. Patent No. 5,304,592 (provided by Safas Corp.).

Table 2

ID	Crosslinked Polymer	Thermoplastic Material	Sheet Extrusion	Sheet Appearance
3A	Ex 1A (35%)	Ex 2 (65%)	Crosslinked particles melted into matrix	No granite texture
3B	Ex 1B (35%)	Ex 2 (65%)	Good processing	Granite texture and smooth surface
3C	Ex 1C (35%)	Ex 2 (65%)	Poor process, stranding and pelletizing problems	Rough surface
3D	Ex 1D (37%)	Ex 2 (63%)	Good processing	Granite texture and smooth surface
3E**	"C" Particles ^a (7-8%)	Ex 2 (92-93%)	No processing problems	Speckled texture with haziness*
3F**	"C" Particles ^a (25%)	Ex 2 (75%)	Majority of particles melted into matrix	Poor granite texture and poor particle/matrix differentiation*
3G**	"C" Particles ^a (32%)	Ex 2 (68%)	stranding and pelletizing problems	opaque*
3H	Ex 1B/1D (< 10%)	Ex 2 (>90%)	Good processing	Transparent, little or no granite texture
3J	Ex 1B/1D (>45%)	Ex 2 (<55%)	Poor process, stranding and pelletizing problems	Rough surface
3K	Ex 1E (25-35%)	Ex 2 (65-75%)	Good processing	No granite texture

* = appearance from Carver press "button"

** = comparative composite plastic composition, not of the present invention

^a = thermoplastic/thermoset particles from Safas Corp., -25+35 ANN

10

Example 4 Physical Properties of Composite Plastic Compositions

Composite plastic compositions based on different crosslinked polymers (prepared according to Example 1) and the thermoplastic matrix material of

Example 2 were fabricated into test samples of sheet (injection molding and sheet extrusion) or film (Carver press) and evaluated for overall appearance and impact strength.

The Falling Dart [dart: 1.36 kilogram (3-pound), 0.63 centimeter, cm (0.25 inch, in) radius; sample of 15.2 cm (6 in) x 15.2 cm (6 in) x 0.32 cm (0.125 in)] and Notched Izod (23°C, 73°F) tests were conducted according to ASTM method D256 (published by the American Society for Testing and Materials) as measures of impact strength.

10

Table 3

Composite Plastic Composition	Falling Dart Impact Test Total energy, joules (foot-pounds)	Notched Izod joule/centimeter (foot-pound/inch)
Ex 1B/1D (15%)/Ex 2 (85%)	10.4 (7.7)	0.42 (0.79)
Ex 1B/1D (30-37%)/Ex 2 (63-70%)	3.9 (2.9)	0.29-0.30 (0.54-0.56)

In addition to the sheet extrusion process used to evaluate the "granite-like" effect, the appearance of the compounded composite material was also visually examined using a "button" prepared on a Carver press according to the following conditions: 65 grams of composite plastic composition pellets were placed in an "X" configuration in a 12.7 cm x 12.7 cm x 0.25 cm thick (5 in x 5 in x 0.1 in thick) aluminum mold between chrome-plated plates; the press was subjected to 1 minute preheat at 188°C (370°F) under 3.45×10^6 pascals (Pa) pressure (500 pounds per square inch/psig), 1 minute heat at 188°C (370°F) under 8.27×10^7 Pa (12,000 psig) and 1 minute cool at 10°C (50°F) under 8.27×10^7 Pa (12,000 psig). The appearances of the Carver press "buttons" for composite plastic compositions of the present invention and that of the prior art were consistent with those described in Table 3 for Examples 3D and 3G, respectively.

COMPOUNDED POLY(1,3-PHENYLENE TEREPHTHALATE)

CLAIMS

We claim:

1. A composite plastic composition comprising a particulate crosslinked polymer dispersed within a thermoplastic matrix, wherein:
 - 5 (a) the composite plastic composition is comprised of 10 to 45 weight percent of the crosslinked polymer, based on weight of the composite plastic composition, and the crosslinked polymer has a particle size substantially from 0.2 to 1.2 millimeters;
 - 10 (b) the crosslinked polymer is comprised of 0.1 to 15 weight percent inert filler and 0.1 to 20 weight percent crosslinker, based on total weight of crosslinked polymer; and
 - 15 (c) the crosslinked polymer is visually differentiable from the thermoplastic matrix.
2. The composite plastic composition of claim 1 wherein the thermoplastic matrix comprises 50 to 100 weight percent poly(alkyl (meth)acrylate) and zero to 50 weight percent impact modifier, based on weight of thermoplastic matrix.
3. The composite plastic composition of claim 2 wherein the poly(alkyl (meth)acrylate) comprises a copolymer of 80 to 99 weight percent methyl methacrylate monomer units and 1 to 20 weight percent (C₁-C₁₀)alkyl acrylate monomer units, based on total weight.
4. The composite plastic composition of claim 2 wherein the impact modifier is a multi-stage sequentially-produced polymer comprising at least three stages in a sequence of a non-elastomeric first stage, an elastomeric second stage and a non-elastomeric third stage.
- 25 5. The composite plastic composition of claim 4 wherein the multi-stage polymer is an emulsion polymer comprising monomer units of methyl methacrylate in the first stage, monomer units selected from one or more of butadiene, styrene and (C₁-C₈)alkyl acrylates in the second stage, and monomer units selected from one or more of (C₁-C₄)alkyl methacrylates, styrene and acrylonitrile in the third stage.

6. The composite plastic composition of claim 1 wherein the crosslinked polymer comprises 90 to 99.5 weight percent monomer units selected from one or more of vinylaromatic monomer and (meth)acrylic monomer and 0.5 to 10 weight percent crosslinker, based on weight of crosslinked polymer.

5 7. The composite plastic composition of claim 6 wherein the (meth)acrylic monomer is selected from one or more of methyl methacrylate, methyl acrylate, ethyl acrylate, acrylic acid and butyl methacrylate.

8. The composite plastic composition of claim 1 wherein the crosslinker is selected from one or more of allyl methacrylate, ethylene glycol dimethacrylate
10 and divinylbenzene.

9. The composite plastic composition of claim 1 wherein the inert filler is selected from one or more of titanium dioxide, iron oxide, alumina, pigments, carbon black and silica.

10. The composite plastic composition of claim 1 wherein the particle size of the crosslinked polymer is substantially from 0.3 to 1.2 millimeters.

15 11. A composite plastic composition comprising a particulate crosslinked polymer dispersed within a thermoplastic matrix, wherein:

20 (a) the composite plastic composition is comprised of greater than 20 to 40 weight percent of the crosslinked polymer, based on weight of the composite plastic composition, and the particle size of the crosslinked polymer is substantially from 0.3 to 1.2 millimeters;

25 (b) the crosslinked polymer is comprised of (i) from 95 to 99.5 weight percent (meth)acrylic monomer units selected from one or more of methyl methacrylate, ethyl acrylate and acrylic acid; (ii) from 0.5 to 5 weight percent crosslinker units selected from one or more of allyl methacrylate, ethylene glycol dimethacrylate and divinylbenzene; and (iii) from 0.3 to 5 weight percent inert filler selected from one or more of titanium dioxide, iron oxide, alumina, carbon black and silica, based on total weight of crosslinked polymer;

30 (c) the thermoplastic matrix is comprised of (i) 50 to 60 weight percent poly(alkyl (meth)acrylate) comprising a copolymer of 80 to 99 weight percent methyl methacrylate monomer units and 1 to 20 weight percent

(C₁-C₁₀)alkyl acrylate monomer units, based on weight of poly(alkyl (meth)acrylate); and (ii) 40 to 50 weight percent impact modifier comprising a multi-stage sequentially produced polymer, based on weight of thermoplastic matrix; and

5 (d) the crosslinked polymer is visually differentiable from the thermoplastic matrix.

12. A process for preparing a composite plastic composition comprising:

10 (a) preparing a crosslinked polymer comprising 0.1 to 15 weight percent inert filler and 0.1 to 20 weight percent crosslinker, based on weight of crosslinked polymer;

15 (b) comminuting the crosslinked polymer to particles having a particle size substantially from 0.2 to 1.2 millimeters;

(c) dispersing 10 to 45 weight percent of the particles of crosslinked polymer within 55 to 90 weight percent of a thermoplastic matrix by a heat processing treatment; and

18 (d) recovering the composite plastic composition as a particulate material.

13. The process of claim 12 wherein the particles of step (b) have a particle size substantially from 0.3 to 1.2 millimeters.

20 14. The process of claim 12 wherein the heat treatment is selected from the group consisting of melt extrusion, coextrusion, blow molding, sheet forming and hot-melt batch mixing.

15. A composite plastic composition prepared according to claim 12.

23 16. A process for preparing a simulated mineral article comprising heat treatment of the composite plastic composition of claim 1 into a physical form selected from the group consisting of sheet, laminated sheet and molded material.

17. The process of claim 16 wherein the heat treatment is selected from the group consisting of melt extrusion, coextrusion, blow molding, sheet forming and 30 thermoforming.

18. An article of manufacture comprising an extruded sheet material resulting from extrusion of the composite plastic composition of claim 1.

19. An article of manufacture comprising a thermoformed product of the composite plastic composition of claim 1.

PLASTIC COMPOSITIONS HAVING MINERAL-LIKE APPEARANCE

ABSTRACT OF THE DISCLOSURE

5 Composite plastic compositions based on the dispersion of selected crosslinked polymers in certain thermoplastic matrices are disclosed. The composite compositions are readily formed and processed by thermal extrusion processes versus conventional casting processes. Preferred composite plastic compositions based on crosslinked poly(alkyl (meth)acrylate) polymers and

10 modified poly(alkyl (meth)acrylate) thermoplastics are especially useful in the preparation of synthetic architectural materials having a mineral-like appearance, such as that of granite.

2000-07-27 09:50:09

